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SYNTHESIS AND CHARACTERISATION OF VANADIUM ANTIMONY OXIDE CATALYSTS

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By

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UPM

Dedicated to my beloved family and friends.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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March 2002

Chairman: Taufiq Yap Yun Hin, Ph.D.

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V-Sb-oxide catalysts are commercially viable catalysts for the ammoxidation of propane to acrylonitrile, a novel and considerable cost saving route compared to the current industrial method which utilizes the ammoxidation of propene. The characteristic of V-Sb-oxide catalysts were studied and analyzed in relation to their structural/composition features using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Brunauer-Emmett-Teller (BET) surface area, Scanning Electron Micrograph (SEM), Energy Dispersive X-ray (EDX) microanalysis and Thermogravimetric Analysis (TGA). Results showed significant difference in presence of crystalline phases, surface area, porosity and morphologies in the samples prepared according to three different methods, i.e. solid state (SS) reaction, sol-gel (GS) and deposition on antimonic acid (DAA) methods, as a function of the Sb:V ratio and heat treatment. XRD and FTIR studies revealed that the calcination temperature at 500 °C is not suitable for the V-Sb-oxide catalysts as there is little or no $VSbO_4$ formed in some samples. Sb/V ratio of 2 or more is recommended for the GS method as there is hardly any Sb species formed for samples

with Sb/V ratio = 1. For the SS method, sample calcined at 700 °C with Sb/V ratio = 1 would be deemed the best as it has the highest amount of $VSbO_4$. Raising of calcination temperature had a detrimental effect on the surface area of the GS and DAA catalysts but bore no significant effect on SS catalysts. The EDX microanalysis showed antimony enrichment on the surface the catalysts. The study of TPD revealed the evolution of lattice oxygen from the catalysts. In TPR, the amount of oxygen desorbed from the catalysts prepared by SS method is found to be much higher compared to the other methods, i.e. about 16.7 times higher than GS method and 6.3 times higher than DAA method (for Sb/V = 1) whilst for ratio 3, it is 21.3 times higher than GS method and 14.5 times higher than DAA method.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN MANGKIN VANADIUM ANTIMONI OKSIDA

Oleh

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Mangkin V-Sb-oksida adalah mangkin yang mempunyai potensi yang baik dalam pasaran untuk proses pengammoksidaan propana kepada akrilonitril. Ia adalah lebih ekonomi berbanding dengan penggunaan propena dalam proses tersebut. Ciri-ciri mangkin V-Sb-oksida dikaji and dianalisis struktur dan komposisinya dengan mengguna teknik seperti pembelauan sinaran-X, spektroskopi inframerah, teknik Brunauer-Emmett-Teller, mikroskopi elektron pengimbas, mikroanalisis tenaga penyebaran sinaran-X dan analisis termogravimetri. Hasil kajian menunjukkan perbezaan dalam fasa kristal, luas permukaan, keliangan dan morfologi dalam mangkin-mangkin tersebut yang disediakan berdasarkan tiga cara berlainan, iaitu, tindakbalas keadaan pepejal (SS), sol-gel (GS) dan pemendakan ke atas asid antimonik (DAA), dengan pembedaan dalam fungsi Sb:V and tindakan haba. Daripada kajian menggunakan teknik pembelauan sinaran-X serta spektroskopi inframerah, didapati tindakan haba pada 500 °C tidak sesuai untuk mangkin V-Sb-oksida kerana sedikit atau tiada $VSbO_4$ terbentuk dalam sampel-sampel. Sb/V sama atau lebih besar daripada 2 adalah baik untuk teknik GS kerana hampir tiada Sb yang terbentuk dalam sampel untuk Sb/V = 1. Untuk teknik SS,

sampel yang ditindakkan haba pada 700 °C dengan Sb/V = 1 dijangka terbaik kerana terdapat jumlah terbesar $VSbO_4$. Peningkatan dalam suhu tindakan haba memberi kesan negatif ke atas luas permukaan mangkin tetapi tidak memberi kesan yang ketara ke atas mangkin SS. Mikroanalisis tenaga penyebaran sinaran-X pula menunjukkan perkayaan unsur antimoni pada permukaan mangkin. Kajian Penyaherapan berprogram suhu (TPD) untuk oksigen menunjukkan pembebasan oksigen kekisi dari mangkin. Dalam kajian Penurunan berprogram suhu (TPR) dalam hydrogen, jumlah oksigen yang ternyaherap dari mangkin yang disediakan melalui teknik SS adalah lebih besar berbanding mangkin-mangkin teknik lain, iaitu hampir 16.7 kali lebih besar berbanding mangkin teknik GS dan 6.3 kali lebih besar berbanding mangkin teknik DAA (untuk Sb/V =1) manakala untuk Sb/V = 3, ia adalah 21.3 kali lebih besar daripada mangkin teknik GS dan 14.5 kali lebih besar berbanding mangkin teknik DAA.

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Last but not least, she would like to dedicate this project to her family members and friends for their prayers, love and moral support.

I certify that an Examination Committee met on 1st March, 2002 to conduct the final examination of Ita Jong Yee Ping on her Master of Science thesis entitled "Synthesis and Characterisation of Vanadium Antimony Oxide Catalysts" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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ITA JONG YEE PING

Date: 9 March 2002

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LIST OF ABBREVIATIONS

ASAP	Analysis of Surface Area and Porosity
DAA	Deposition on Antimonic Acid Method
E_d	Desorption activation energy
EDX	Energy Dispersive X-ray Microanalysis
E_r	Reduction activation energy
FID	Flame ionization detector
FTIR	Fourier Transform Infra-Red
GS	Gel-Solid Method
JCPDS	Joint Committee on Powder Diffraction Standards
MS	Mass spectroscopy
OFN	Oxygen free nitrogen
SEM	Scanning Electron Micrograph
SS	Solid State Reaction Method
STP	Standard temperature and pressure
TCD	Thermal conductivity detector
TGA	Thermogravimetric Analysis
TPD	Temperature-Programmed Desorption of Oxygen
TPR	Temperature-Programmed Reduction in Hydrogen
VSbO	Vanadium Antimony Oxide
XRD	Powder X-Ray Diffraction Analysis

CHAPTER 1

INTRODUCTION

Selective catalytic oxidation and ammoxidation processes of hydrocarbons comprise approximately one quarter of the value produced by all catalytic processes worldwide. They contribute hence significantly to the gross national product of industrial countries and afford future opportunities for developing countries [1]. Oxidation processes are defined as conversions of compounds under the influence of various oxidizing agents. There are two types of oxidation, i.e. complete and partial oxidation. Complete oxidation is an undesirable side process in organic synthesis which leads to the formation of CO, CO_2 and H_2O, whereas partial oxidation processes involves usage of air or oxygen in the manufacture of chemicals [2].

Oxidation reactions are made much more selective in nature by means of a catalyst that lowers the activation energy for the selected process and provides a facile path by which useful products can form. There are three categories of catalysts for oxidation reactions, i.e. transition metal oxides in which oxygen is readily transferred to and from the structure, metals onto which oxygen is chemisorbed, and metal oxides in which the active species is chemisorbed oxygen, as molecules or atoms [2].

There are two types of selective oxidation reactions. Firstly, the dehydrogenation reactions, in which a hydrocarbon molecule is converted into a more unsaturated

hydrocarbon by the breaking of C-H bonds and forming of C=C bonds. Secondly, the dehydrogenation and oxygen insertion, in which oxygen is needed as an oxidant for the incorporation into the hydrocarbon molecules and in the formation of water in the dehydrogenation steps. In general, the C-H bonds are broken and C-O bonds are formed [3].

Selective oxidation often requires catalysts of a more complex nature. Theoretically, a metal could be used for the catalysis process but it would not be favourable if high temperature is needed as the hydrocarbon is often unstable and might decompose completely. A successful process can only result if the thermodynamics allow the use of a somewhat lower temperature for favourable reaction to take place. It is of paramount importance to find catalysts that can conduct the catalysis reaction selectively, i.e. without giving deep oxidation at the same time. In the oxidation of hydrocarbons by incorporation of one or more oxygen atoms, it is usually important to preserve the original unsaturation, and to activate one of the carbon-hydrogen bonds instead [4].

The first major breakthrough in the search for an acceptable catalyst for selective oxidation occurred in the late 1950s when it was discovered in the Sohio laboratories that a compound oxide, namely bismuth molybdate, showed an acceptably high selectivity in the oxidation of propene to acrolein [4]:

$$C_3H_6 + O_2 \rightarrow H_2C{=}CH\text{-}CHO + H_2O \qquad [1\text{-}1]$$

This was soon followed by an even more important finding that propene could be oxidized in the presence of ammonia in a one-step ammoxidation to give acrylonitrile:

$$C_3H_6 + NH_3 + 3/2\ O_2 \rightarrow H_2C{=}CH\text{-}CN + 3H_2O \qquad [1\text{-}2]$$

Some of the common oxide-catalyzed selective oxidation reactions can be seen in Table 1 [3]:

Table 1: Common oxide-catalyzed selective oxidation reactions

Reactions	**Catalysts**
1. Dehydrogenation	
ethylbenzene→ styrene	V-Ti-O
isopentane, isopentene→isoprene	Sn-Sb-O
Butane, butene→butadiene	Bi-Mo-O, promoted Fe-O, promoted V-O
Methanol→formaldehyde	Fe-Mo-O, MoO_3
2. Dehydrogenation and Oxygen Insertion	
Butane, butene→maleic anhydride	V-P-O
Propene→acrolein (Propene and NH_3→acetonitrile)	Bi-Mo-O Bi-Mo-O, U-Sb-O, Fe-Sb-O, Bi-Sb-Mo-O
methane→methanol, formaldehyde	Mo-O, V-O
ethylene→ethylene oxide	Fe-Mo-O
methyl ethyl ketone→acetaldehyde, acetic acid	V-Mo-O

Due to the global abundance of liquefied petroleum gas (LPG), interest in the potential of light alkanes as sources in selective oxidation to their corresponding useful products is increasing. Among these is the partial oxidation and ammoxidation of propane to acrylonitrile.

Acrylonitrile

Acrylonitrile is commodity chemical used throughout the world to make acrylic fibers for shirts, socks, sweaters, carpets, blankets; plastics for computers, telephones, refrigerators, food packaging and cars; nitrile rubber for automotive tyres, hoses and belts; and a variety of specialty products. About 95 % of the world's production of acrylonitrile uses the BP Amoco Chemicals process [5]. Fabrics account for the large percentage of acrylonitrile end uses (Table 2). Acrylic fibers are a popular substitute for cotton and wool and are used to make carpeting, blankets and especially clothing. Rugged, durable acrylonitrile-butadiene-styrene (ABS) plastics, derived from acrylonitrile, are chosen for telephones, computer and television, housings, sports equipment and molded automobile parts. Oil resistant nitrite rubber, made from acrylonitrile, is used for hoses at gasoline service stations and in automobiles, trucks and buses. BP Amoco Chemical's scientists recover co-products generated by the acrylo process. These co-products, previously treated as unusable wastes, are now used by manufacturers to make household detergents and shampoos, dyes, plastics and pharmaceuticals, including life-saving insulin for diabetics and many other products [5].

Table 2: A summary of usage of acrylonitrile [5]

Usage	Percentage
Co-monomer for acrylic and modacrylic fibers	51 %
Co-monomer for acrylonitrile-butadiene-styrene resins	18 %
Chemical intermediate for adiponitrile	13 %
Chemical intermediate for acrylamide	6 %
Co-monomer for nitrile elastomers	3 %
Co-monomer for Styrene-Acrylonitrile resins	2 %
Other uses	7 %

Acrylonitrile capacity amounted to 10.0 billion pounds as of 1st January, 1995 [7]. The growth of its demand was 2.2 % per year. The expectant growth was projected to be 2 % per year through 2001 [8].

World acrylonitrile consumption is largely dependent on demand for acrylic fibers, especially in Asia and Europe, where acrylic fibers account for 50 % of consumption. In contrast, acrylic fibers account only for 25 % of acrylonitrile demand in the United States. Combined, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins account for 24 % of world consumption of acrylonitrile, although in Asia they account for 34 % of demand. Acrylamide accounts for most of the growth in the 'other' category. Future demand growth for acrylonitrile will come mainly from acrylic fibers (Asia and Eastern Europe), ABS/SAN (Asia) and acrylamide (all regions) [9].

In the long term, developing Asian countries possess the best conditions for continued growth of acrylonitrile consumption. Taiwan, China and India will continue to be short of acrylonitrile requirements for at least the next 5 years and will continue to rely on imports to satisfy demand, mainly for acrylic fiber production. Additionally, as production of ABS/SAN resins continues its shift to Asia, demand for acrylonitrile for this application will grow at robust rates. Demand for acrylonitrile in Eastern Europe is forecasted to grow aggressively, due mainly to healthier utilization rates at existing acrylic fiber plants after years of negative growth and low utilization rates [9].

Production of Acrylonitrile

Over 90 % of world acrylonitrile is produced by using the SOHIO Acrylonitrile Process [7]. This process is based on vapour phase catalytic air oxidation of propene and ammonia, known as ammoxidation, in a fluid bed reactor [10].

$$CH_2{=}CH\text{-}CH_3 + NH_3 + 3/2\ O_2 \xrightarrow[300\text{-}450\ ^\circ C]{\text{*Catalysts}} CH_2{=}CH\text{-}CN + 3H_2O \qquad [1\text{-}3]$$

*Catalysts: $BiO_2.nMoO_3$ (n = 1,2,3)
USb_3O_{10}
Fe_2O_3/Sb_2O_4
$Bi/Mo/O_x$ multicomponent systems

What about Propane as Feedstock?

The difference between propane and propene prices, i.e. 3 - 15 cents a pound, is the reason behind the interest in developing technology to use propane instead of propene as feedstock. The use of this technology appears to be most promising in the Far East where propane is more readily available than propene [11].

Acrylonitrile Production via Propane Ammoxidation Route

When considering the selective catalytic oxidation of propane into oxygenates, two main difficulties arise. The first one is, as for the partial oxidation of other light alkanes, the lower reactivity of the reactant as compared to that of the formed products. Activation of the reactant needs operating conditions (temperature as high as 500 °C for example) which are detrimental to the stability of the product. Therefore, the considered reaction requires catalysts with specific properties: activation of propane partial oxidation and decrease or inhibition of the product oxidation. The second difficulty is to design suitable catalysts because little is known about the involved reaction mechanisms [12].

$$CH_3\text{-}CH_2\text{-}CH_3 + NH_3 + 2O_2 \rightarrow CH_2{=}CH\text{-}CN + 4H_2O \qquad (\Delta H = -151 \text{ kcal/mol}) \quad [1\text{-}4]$$

It was found that two main classes of catalysts give the best results:

- Systems based on antimonate rutile structure and containing V as the key element [13, 14];
- Systems based on the Bi-Mo-V scheelite structure [15].

Fe-antimonate containing excess Sb-oxide and SnO_2-Sn_2O_x are known system for propene ammoxidation [16] but they show poor activity/selectivity for propane ammoxidation [17]. Other catalysts studied included Ga antimonate [18], Ag-doped bismuth vanadomolybdate [19], V-silicate and V-aluminium phosphate [20] and vanadyl pyrophosphate [17] Best performance is obtained using V-antimonate systems which contain excess Sb-oxide [21]. The first patent reports selectivity in acrylonitrile of approximately 60 % [22].

In 1988, Standard Oil (now BP America) published 5 key patents on V-Sb-O based catalyst, reporting much better yields and productivities in acrylonitrile from propane. In 1996, BP Amoco started off a demo unit for production of acrylonitrile using propane in its plant in Green Lake, USA. The process is said to cut cost by at least 20 % [23].

Vanadium Antimony Oxide (V-Sb-O) Catalyst

The phase composition of V-Sb-oxide catalysts depends on four main factors: (i) method of preparation, (ii) temperature, (iii) gas phase composition during the thermal treatment, (iv) Sb/V atomic ratio [24].